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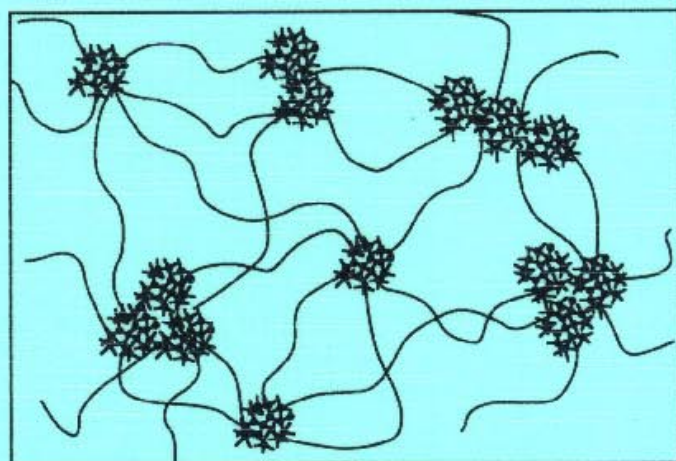
Soft Chemistry Routes to New Materials

- Chimie Douce -

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Front cover illustration (book edition):

Soft Chemistry deals with intercalation-deintercalation reactions (lower left), grafting-pillaring (lower right), polycondensation of solid units or molecules through acid-base reactions and sol-gel processes (lower middle). The latter can end up with mixed inorganic organic constructions (upper part).

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PARTIAL CHARGES DISTRIBUTIONS IN CRYSTALLINE MATERIALS THROUGH ELECTRONEGATIVITY EQUALIZATION

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Keywords: Electronegativity, Partial Charge Model, Madelung Potentials, Oxides, Solid-State Acidity

ABSTRACT : A structure-dependent version of Sanderson's electronegativity equalization principle allowing a rapid computation of partial charges distributions in crystalline solids is described. The method is first applied to simple oxides ranging from highly ionic 3D-networks (Li_2O , CaO) to highly covalent molecular crystals (P_4O_{10} , OsO_4), then to more complex structures based on polymerized anionic ($\text{K}_2\text{Ti}_4\text{O}_9$) or cationic (zunyite $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH})_{18}\text{Cl}$) frameworks. From these partial charges distributions, it becomes possible to quantify the solid-state acid-base chemistry as a function of any crystalline or molecular environment.

1. INTRODUCTION

The accurate knowledge of partial charges distributions in solid materials is of the utmost importance to get a better understanding of their solid-state chemical reactivity. Unfortunately, *ab initio* computations are not well suited to a solid-state approach, requiring huge computers. The aim of this contribution is to show that a structure-dependent version of the electronegativity equalization principle of R.T. Sanderson [1] allows to compute quite detailed partial charges distributions in crystalline solids. The algorithm is based on a formula derived from Density Functional Theory by W.J. Mortier et al [2,3] that we have matched to the Sanderson electronegativity scale :

$$\left\{ \begin{array}{l} \chi_i = \langle \chi \rangle = \chi_i^0 + k_1 \sqrt{\chi_i^0} q_i + k_2 \sum_{j=1}^n M_{ij} q_j \quad \forall i = 1, \dots, n \\ \sum_{i=1}^n q_i = 0 \end{array} \right. \quad k_1 = 2.415 \text{ and } k_2 = 2.415 \text{ \AA} \quad (1)$$

$$M_{ij} = \frac{14400\pi R^2}{V} \sum_{\alpha \leq 2\pi R|\vec{h}|} \exp[2\pi i \vec{h} \cdot (\vec{x}_j - \vec{x}_i)] \frac{[\alpha \cos \alpha - 3 \sin \alpha + 2\alpha]^2}{\alpha^{12}} - \frac{25}{14R} \delta_{ij}$$

$$\vec{h} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

$$\vec{x} = x\vec{a} + y\vec{b} + z\vec{c}$$

In these relationships, χ_i^0 and q_i are the dimensionless Sanderson electronegativity and partial charge of the i^{th} atom in the unit cell which contains n non-equivalent atoms, $\langle \chi \rangle$ the mean electronegativity of the network to which all individual electronegativities χ_i

have to equal and k_1 , k_2 empirical calibration constants [4]. M_{ij} is the Madelung contribution at site i coming from all sites j in the network. It is computed in the reciprocal space following the method of F. Bertaut [5] and R.E. Jones & D.H. Templeton [6], knowing the unit cell parameters, the atomic coordinates \bar{x}_i , \bar{x}_j of sites i or j and R the minimum interatomic distance in the structure. The dimensionless summation index α is defined as $\alpha = 2\pi|\bar{h}|R$, where $|\bar{h}|$ stands for the modulus of any reciprocal space vector and δ_{ij} is the Kroenecker symbol. Knowing the electronegativities and each M_{ij} allows to compute the $(n+1)$ unknowns (n partial charges and the mean electronegativity $\langle\chi\rangle$) by solving the linear system (1). This method have been used to calculate partial charges distributions in oxide-based materials. Knowing partial charges on oxygen atoms $q(O)$, pK_a values are then calculated using equation 2 [4] :

$$pK_a(O) = -42.2q(O) - 19.8 \quad (2)$$

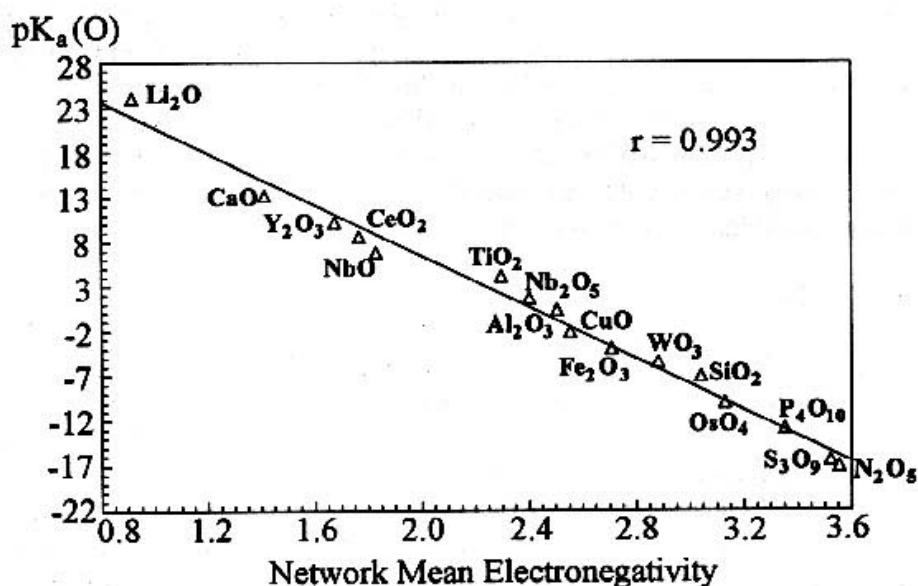


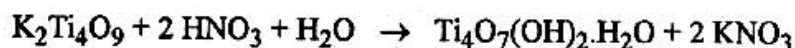
Figure 1 : Theoretical acidity constants (pK_a) of oxide networks against their calculated mean electronegativity. pK_a values for non-equivalent oxygen atoms within the same structure have been properly averaged.

2. RESULTS

Various oxides ranging from highly ionic 3D-networks to highly covalent molecular crystals have first been investigated (figure 1). When oxygen atoms are in eightfold coordination (Li_2O , Na_2O , K_2O) they display strong basic properties ($pK_a > 14$). Conversely, when they are found in terminal position (OsO_4 , N_2O_5) they display strong acid behavior ($pK_a < -10$). Generally speaking, oxygen atoms become more and more acidic as their coordination number decreases. For example, with MO oxides the pK_a values as a function of the metal atom are found to be : 13.5 (Sr), 13.2 (Ca), 12.7 (Ba), 9.3 (Mg), 6.8 (Nb), 6.0 (Be), 1.6 (Mn), -2.0 (Cu), -5.4 (Zn), -6.7 (Hg). For a fixed coordination number, pK_a values decreases as the electronegativity of the metal atom increases. Thus for M_2O_3 corundum-type structure (R-3c) we found : 6.1 (Ti), 0.3 (Al), 0.5 (V), -1.0 (Cr) and -4.0 (Fe). However, if we change the structural type, inversions may occur : $\chi(Al) > \chi(Mn)$ but $pK_a(Al_2O_3) = 0.3$ (R-3c) $>$ $pK_a(Mn_2O_3) = -0.1$ (Ia3).

When both the metal atom and the stoichiometry are kept constant, no simple rules can be found. Taking the TiO_2 polymorphs as a test we found pK_a : 4.5 ($\text{TiO}_2\text{-B}$), 4.1 (anatase), 4.0 ($\text{TiO}_2\text{-II}$), 3.95 (rutile) and 3.9 (brookite). Finally, if within the same structure, several atoms are found in different crystalline environments, the lower the coordination, the higher the acidity. Typical examples are found for molecular crystal: P_4O_{10} [-12.1 (μ_2), -13.6 (t)], Mn_2O_7 [-5.0 (μ_2), -8.2 (t)]; chain-like structures: $\beta\text{-SO}_3$ [-15.9 (μ_2), -16.6 (t)], CrO_3 [-5.2 (μ_2), -7.9 (t)]; layered compounds: MoO_3 [-7.2 (μ_3), -8.2 (μ_2), -9.9 (t)], V_2O_5 [-2.5 (μ_3), -3.8 (μ_2), -5.3 (t)]; and 3D networks: $m\text{-ZrO}_2$ [9.3 (μ_4), 8.7 (μ_3)], $\text{B-Nb}_2\text{O}_5$ [2.5 (μ_3), 1.1 (μ_2)].

One of the big advantage of the model is that it applies without any modification to very complex mixed oxides structures. Let us consider a typical example provided by the layered compound $\text{K}_2\text{Ti}_4\text{O}_9$ which can be considered as a $[\text{Ti}_4\text{O}_9]^{2-}$ 3D-polyanion with readily exchangeable K^+ counter-ions [7]. It has been shown [8] that this compound can be hydrolyzed according to :



leading finally to the $\text{TiO}_2(\text{B})$ structure after thermolysis around 500°C . In order to check that potassium atoms were readily exchangeable in this structure and that some oxygen atoms were basic enough to be hydroxylated, we have computed the partial charge distribution on the 60 atoms found in the unit cell of $\text{K}_2\text{Ti}_4\text{O}_9$ (table1).

4.O6 = -0.766	4.O8 = -0.708	4.O5 = -0.703	4.O7 = -0.699	4.O9 = -0.641
4.O3 = -0.629	4.O4 = -0.627	4.O2 = -0.625	4.O1 = -0.620	4.Ti3 = +0.948
4.K1 = +0.983	4.Ti4 = +0.992	4.Ti2 = +0.995	4.K2 = +1.047	4.Ti1 = +1.053

Table 1 : Partial charges distribution in $\text{K}_2\text{Ti}_4\text{O}_9$ computed with electronegativities 3.654 for O, 1.295 for Ti and 0.74 for K, leading to a framework mean electronegativity of 1.726 (Sanderson scale).

As expected it is found that potassium atoms behave as mere counter-ions ($q(\text{K}) \approx +1$) facing a highly covalent $[\text{Ti}_4\text{O}_9]^{2-}$ framework ($q(\text{Ti}) \approx +1 \ll +4$, $\langle q(\text{O}) \rangle \approx -0.67 \gg -2$). Such atoms are thus readily exchangeable with $[\text{H}_3\text{O}]^+$ ions. More interesting is the clear distinction found between the nine oxygen atoms present within the framework. If the charges are converted to pK_a values according to (2) we obtain, in contrast with simple oxides, a totally inverse order as a function of the oxygen coordination number :

$$\text{O6}(t) = 12.5 > [\text{O8}, \text{O5}, \text{O7}](\mu_2) = 9.9 > \text{O9}(\mu_2) = 7.3 > [\text{O3}, \text{O4}, \text{O2}, \text{O1}](\mu_3, \mu_4) = 6.6$$

The rather high pK_a value found for the terminal O6 atom suggests that it must be protonated in contact with water, releasing OH^- ions in solution. Moreover, outer μ_2 -oxo groups (O5, O5 and O8) although less basic, can also be hydroxylated allowing the complete transformation into the $\text{TiO}_2(\text{B})$ structure at high temperature. Finally, the other inner μ_2 -oxo (O9), μ_3 -oxo (O3) and μ_4 -oxo (O4, O2 and O1) groups are quasi-neutral and should not react with water.

To conclude, we would like to investigate another kind of complex oxide network found in the mineral zunyite and having an ideal formula $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH})_{18}\text{Cl}$ [9].

Formally this structure can be derived from a 3D-polycationic octahedral network $[\text{Al}_{13}\text{O}_4(\text{OH})_{18}]^{13+}$ having a building unit closely related to the well-known tridecameric polycation $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+}$ found in hydrolyzed Al^{3+} solutions [10]. Within the voids generated by the tetrahedral packing of these polymerized tridecameric units, discrete pentameric polyanions $[\text{Si}_5\text{O}_{16}]^{12-}$ and monomeric chloride ions insure charge compensation. Table 2 gives the total partial charge distribution computed on the 300 atoms found in the unit cell of zunyite.

24.O3 = -0.642	48.O4 = -0.489	16.O1 = -0.471	48.O5 = -0.404
16.O2 = -0.376	4.Cl = -0.335	48.H1 = +0.245	24.H2 = +0.426
4.Si1 = +0.514	16.Si2 = +0.520	4.Al1 = +0.747	48.Al2 = +0.788

Table 2 : Partial charges distribution in zunyite computed with electronegativities 3.654 for O, 3.475 for Cl, 2.592 for H, 2.138 for Si and 1.714 for Al, leading to a framework mean electronegativity of 2.660 (Sanderson scale).

The highly covalent nature of this compound is evidenced by its total charge distribution : $[(\text{Al}1)(\text{Al}2)_{12}(\text{O}1)_4(\text{O}3\text{H}2)_6(\text{O}4\text{H}1)_{12}]^{+4.1} \cdot [(\text{Si}1)(\text{O}2)_4(\text{Si}2)_4(\text{O}5)_{12}]^{-3.8} \cdot \text{Cl}^{-0.3}$. Two kind of μ_2 -hydroxo groups bridging two Al atoms are found in this structure : a neutral one $\text{pK}_a(\text{O}3) = 7.3$ and a rather acidic one $\text{pK}_a(\text{O}4) = 0.8$. Other oxygen atoms in the structure have rather low pK_a values : $\text{O}1 = 0.1$ (OAl_4), $\text{O}5 = -2.7$ (OSiAl_2) and $\text{O}2 = -3.5$ (OSi_2) and are thus hardly protonable.

3. CONCLUSION

This work has tried to show that the electronegativity equalization principle can be a very valuable tool in the field of solid-state acid-base chemistry. It is based on a very simple algorithm (relation 1) which can be implemented on any personal computer. Input data are limited to a crystalline structure (space group, asymmetric unit cell parameters and fractional atomic coordinates) and an electronegativity scale (Sanderson, Pauling, Allred-Rochow, Mulliken ...). With this extremely limited data set, quite detailed partial charges distribution can be computed which throw new light on very complex domains such as aqueous [6] or solid-state inorganic chemistry (*vide supra*).

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